Supplementary Materials

Article

Electronic Structure and *d*-Band Center Control Engineering over Ni-doped CoP3 Nanowall Arrays for Boosting Hydrogen Production

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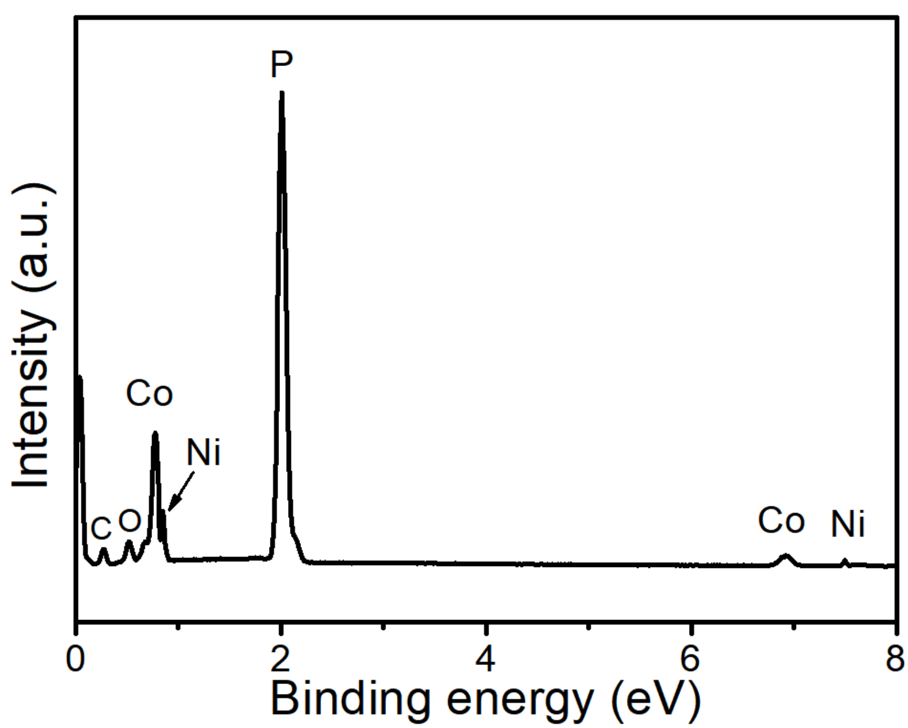

Figure S1. EDX spectrum of Ni-CoP_3-7 NWAs/CC.

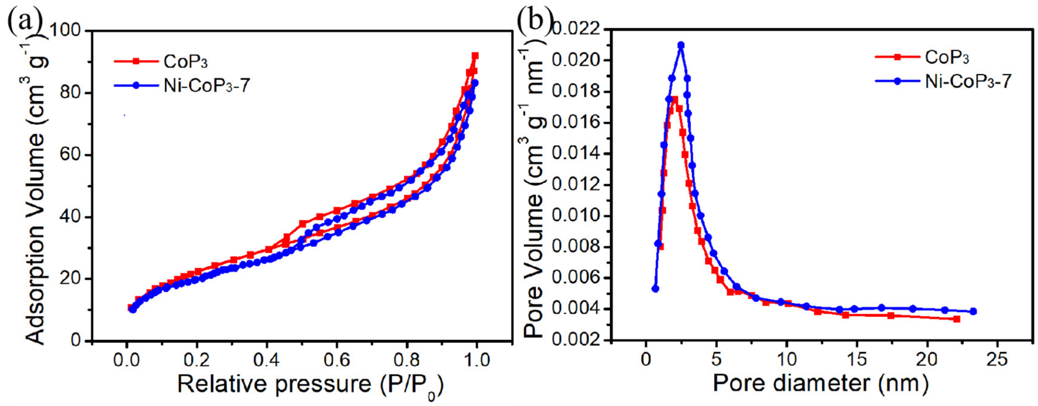

Figure S2. (**a**) Nitrogen adsorption/desorption isotherm and (**b**) the BJH pore-size distribution curve of CoP3 and Ni-CoP_3-7 NWAs, respectively.

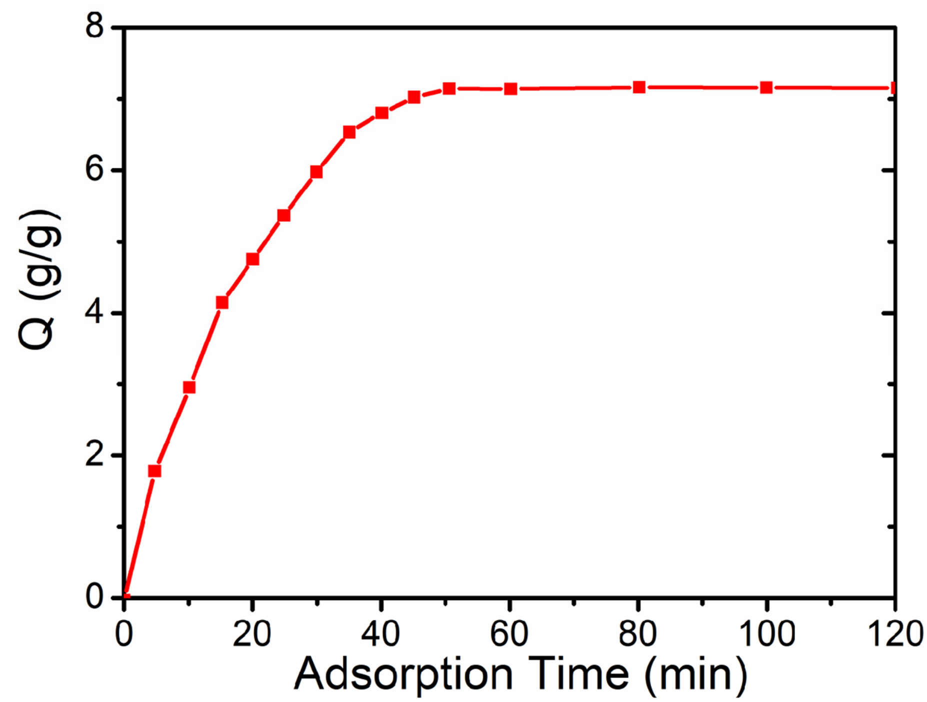

Figure S3. The dependence of the adsorption time on the amount of absorbed H^+ (based on the quality of HCl) on the Ni-CoP_3-7 NWAs catalysts in 5 mM aqueous solution.

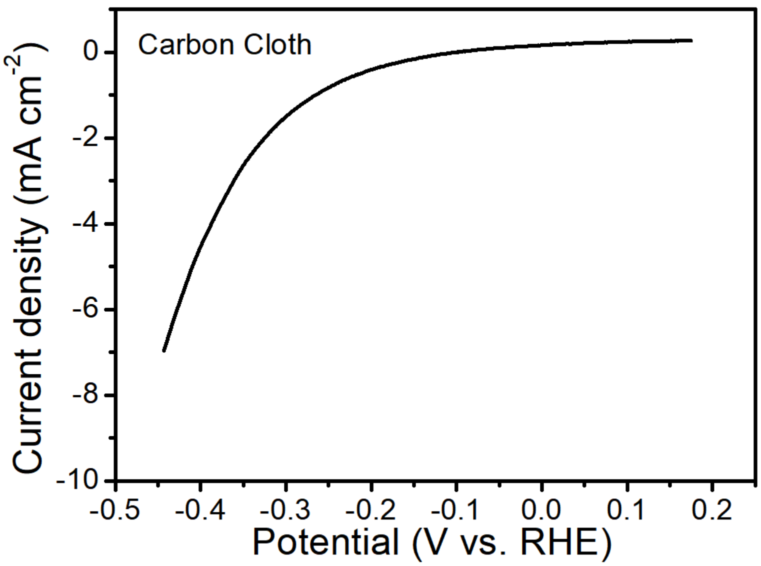

Figure S4. Polarization curves of CC in 0.5 M H_2SO_4.

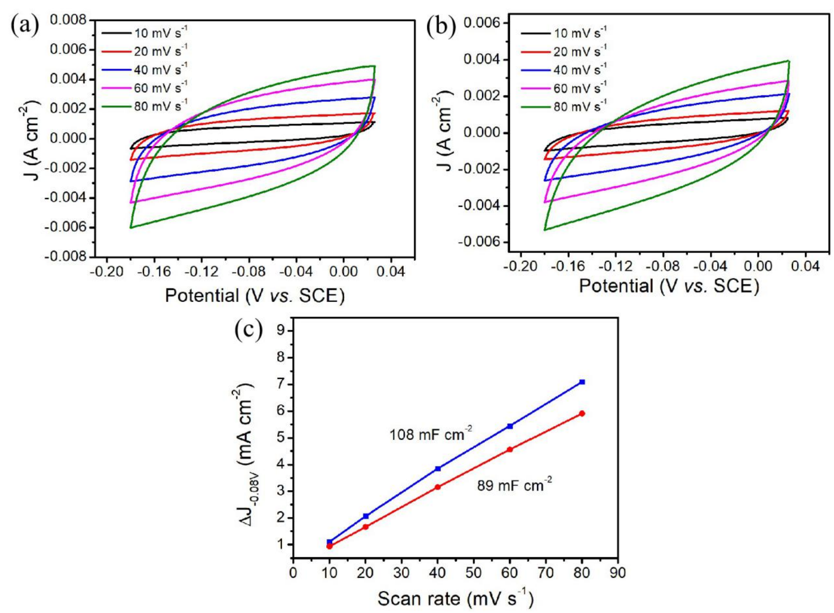

Figure S5. Cyclic voltammograms in the region of -0.18-0.02 V vs. SCE at various scan rates and the corresponding linear fitting of the capacitive currents vs. scan rates to estimate the double layer capacitance: (**a**) Ni-CoP_3-7 NWAs/CC and (**b**) CoP_3 NWAs/CC; (**c**) The capacitive currents were measured at -0.08 V vs. SCE plotted as a function of scan rate.

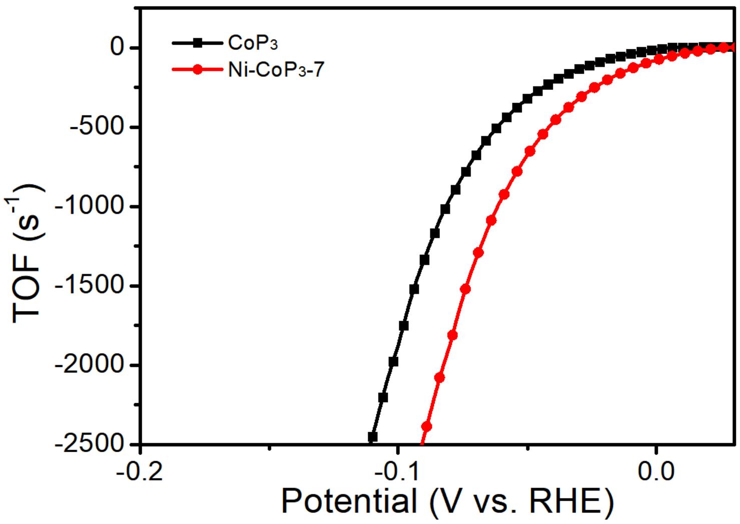

Figure S6. TOF curves of CoP_3 and Ni-CoP_3-7.

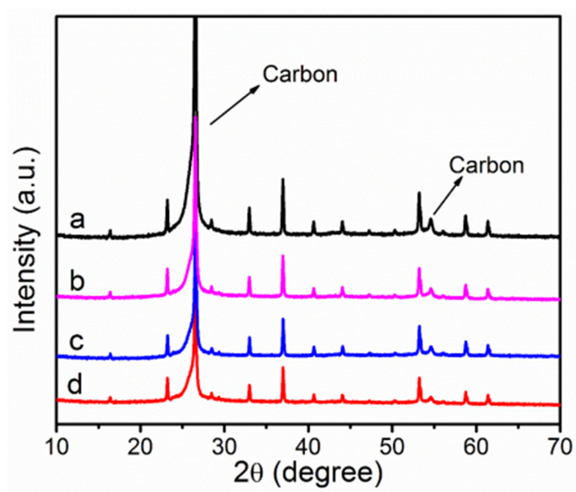

Figure S7. (**a**) XRD patterns of Ni-CoP_3-7 NWAs/CC and (**b–d**) the XRD patterns of Ni-CoP_3-7 NWAs/CC electrode after 5000 cycles CV scanning at pH 0, pH 7 and pH 14, respectively.

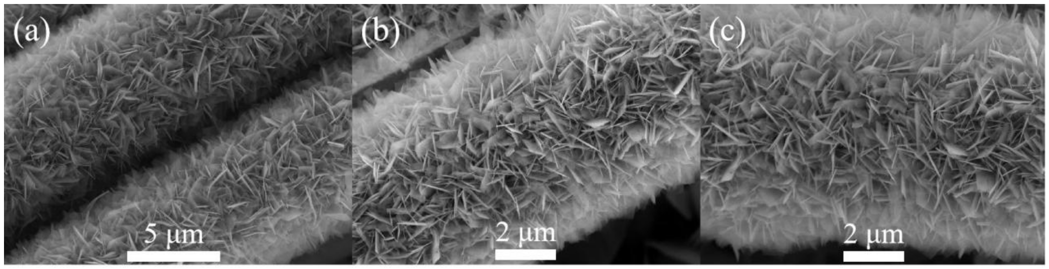

Figure S8. SEM images after 5000 cycles CV scanning at pH 0 (**a**), pH 7 (**b**) and pH 14 (**c**), respectively.

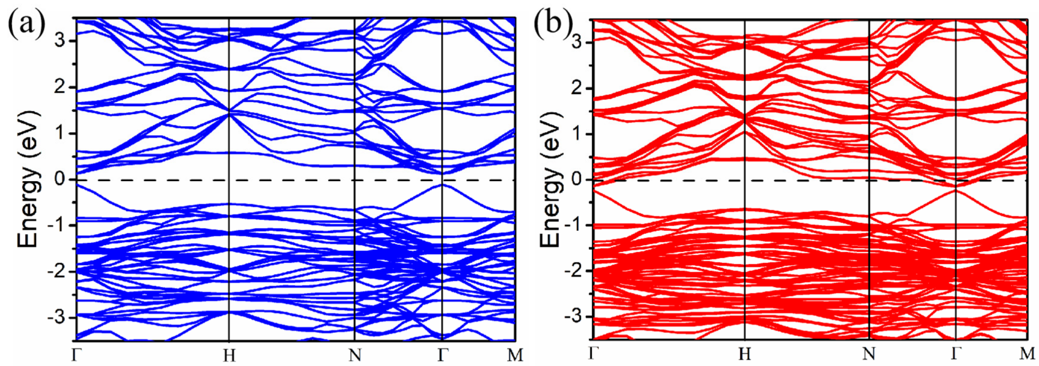

Figure S9. Electronic band structure of (**a**) CoP_3 and (**b**) Ni-CoP_3.

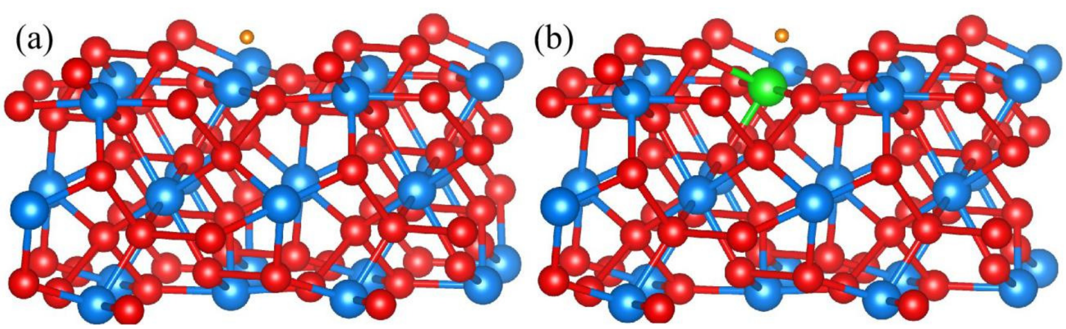

Figure S10. The configuration of hydrogen adsorption on CoP_3 (**a**) and Ni-CoP_3 (**b**).

Table S1. Comparison of HER performance in acid media for CoP_3 HSs/CC with other TMPs HER electrocatalysts.

Catalyst	Onset η (mV)	Current density (*j*, mA cm^{-2})	η at the corresponding *j* (mV)	Exchange current density (mA cm^{-2})	Ref.
FeP nanosheets	100	10	240	-	*Chem. Commun.*, 2013, 49, 6656
FeP NWs/Ti	38	10	55	0.42	*Angew. Chem. Int. Ed.*, 2014, 53, 12855
FeP NWs	-	10	96	0.17	*Chem. Commun.*, 2016, 52, 2819.
FeP NPs	38	10	112	-	*Nanoscale*, 2015, 7, 4400
FeP NAs	-	10	85	-	*J. Mater. Chem. A*, 2014, 2, 17263
FeP_2/C	-	5	500	$1.75*10^{-3}$	*J. Mater. Chem. A*, 2015, 3, 499
Ni_2P NPs	-	20	130	$2.7*10^{-3}$	*J. Am. Chem. Soc.*, 2013, 135, 9267
Ni_2P/graphene	37	10	102	0.049	*J. Power Sources*, 2015, 297, 45
Ni_2P/CNs	40	10	92	-	*J. Power Sources*, 2015, 285, 169
NiP_2/CC	-	10	116	0.26	*Nanoscale*, 2014, 6, 13440
Se doped NiP_2	-	10	84	-	*ACS Catal.*, 2015, 5, 6355
Cu_3P NWs	62	10	143	0.18	*Angew. Chem. Int. Ed.*, 2014, 53, 9577
MoP Bulk	50	30	180	0.034	*Energy Environ. Sci.*, 2014, 7, 2624
MoP NPs	40	10	125	0.086	*Adv. Mater.*, 2014, 26, 5702
MoP_2 NPs/Mo	-	10	143	0.06	*Nanoscale, 2016, 8, 8500*
MoP_2 nanosheets	-	10	58	-	*J. Mater. Chem. A*, 2016, 4, 7169
WP	50	10	120	-	*Chem. Commun.*, 2014, 50, 11026
α-WP_2	54	10	161	0.017	*ACS Catal.*, 2015, 5, 145
β-WP_2	56	10	148	0.013	*J. Power Sources*, 2015, 278, 540
Co_2P	-	10	95	-	*Chem. Mater.*, 2015, 27, 3769
CoP/CC	38	10	67	0.288	*J. Am. Chem. Soc.*, 2014, 136, 7587
CoP NPs	-	20	85	-	*Angew. Chem. Int. Ed.*, 2014, 53, 5427
CoP/CNs	40	10	122	0.13	*Angew. Chem. Int. Ed.*, 2014, 53, 6710
Ni-CoP_3 NWAs	33	10	95	0.217	This work
		100	**177**		

NPs (Nanoparticles); CNs (Carbon Nanotubes); CC (Carbon Cloth); NWs (Nanowires); NAs (Nanoneedle Arrays); CPs (Concave Polyhedrons)

Table S2. Comparison of HER performance in neutral media for Ni-$CoP_{3\text{-}7}$ NWAs/CC with other HER electrocatalysts.

Catalyst	Current density (j, mA cm^{-2})	Potential at the corresponding j (mV)	Ref.
Mo_2B	1	250	*Angew. Chem. Int. Ed.*, 2012, 51, 12703
Mo_2C	1	200	*Angew. Chem. Int. Ed.*, 2012, 51, 12703
Co-S/FTO	2	83	*J. Am. Chem. Soc.*, 2013, 135, 17699
$CuMoS_4$	2	210	*Energy Environ. Sci.*, 2012, 5, 8912
WP	10	200	*ACS Appl. Mater. Interfaces*, 2014, 6, 218740
WP_2	10	298	*J. Power Sources*, 2015, 278, 540
MoP_2 NPs/Mo	10	211	*Nanoscale*, 2016, 8, 8500
CoP NPs	2	65	*J. Am. Chem. Soc.*, 2014, 136, 7587
CoP_3 NPAs	10	138	*Appl. Surf. Sci.*, 2019, 494, 179-186
Ni-CoP_3-7 NWAs	10	129	This work

Table S3. Comparison of HER performance in alkaline media for CoP_3 NPAs/CC with other HER electrocatalysts.

Catalyst	Current density (j, mA cm^{-2})	Potential at the corresponding j (mV)	Ref.
Ni wire	10	350	*ACS Catal.*, 2013, 3, 166
MoB	10	225	*Angew. Chem. Int. Ed*, 2012, 51, 12703
NiP_2	10	102	*Nanoscale*, 2014, 6, 13440
WP	10	250	*ACS Appl. Mater. Interfaces*, 2014, 6, 218740
WP_2	10	225	*J. Power Sources*, 2014, 136, 7587
MoP_2 nanosheets	10	85	*J. Mater. Chem. A*, 2016, 4, 7169
MoP_2 NPs/Mo	10	194	*Nanoscale*, 2016, 8, 8500
CoP nanowires	10	209	*J. Am. Chem. Soc.*, 2014, 136, 7587
CoP_3 NPAs	10	109	*Appl. Surf. Sci.*, 2019, 494, 179-186
Ni-CoP_3-7 NWAs	10	102	This work